

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
21 December 2000 (21.12.2000)

PCT

(10) International Publication Number
WO 00/77292 A1(51) International Patent Classification⁷: D06P 1/52, 3/32

(21) International Application Number: PCT/GB00/02340

(22) International Filing Date: 15 June 2000 (15.06.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
9913947.9 15 June 1999 (15.06.1999) GB(71) Applicant (for all designated States except US): BLC
LEATHER TECHNOLOGY CENTRE [GB/GB];
Leather Trade House, Kings Park Road, Moulton Park,
Northampton NN3 6JD (GB).

(72) Inventor; and

(75) Inventor/Applicant (for US only): HUDSON, Andrew
[GB/GB]; BLC Leather Technology Centre, Leather Trade
House, Kings Park Road, Moulton Park, Northampton NN3
6JD (GB).(74) Agent: BROOKES & MARTIN; High Holborn House,
52-54 High Holborn, London WC1V 6SE (GB).(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE,
DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU,
ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS,
LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO,
NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR,
TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 00/77292 A1

(54) Title: LEATHER DYEING

(57) Abstract: A process for dyeing leather with reactive and acid dyes comprises pre-impregnating the leather with an aminosilane or aminosiloxane that provides additional dye sites in the collagen matrix, allowing deeper dye shades to be obtained. Treatment to polymerise or crosslink the aminosilane or aminosiloxane increases the colour fastness.

WO 00/77292

PCT/GB00/02340

LEATHER DYEING

10/519540
DT01 Rec'd PCT/PTC 28 DEC 2004

This invention is concerned with dyeing leather, and in particular to a process for dyeing leather which achieves improved colour fastness, particularly for deep shades.

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Although some colour may be imparted to leather by the tanning agents during tanning, leather is usually dyed to improve its appearance and to make it saleable. A variety of dyeing procedures are in commercial use, the most commonly used being drum and spray application. The amount of dyestuff used on a leather is dependent on the intended purpose of the leather as well as the required surface shade. For example, with many shoe upper leathers only surface penetration of the dyestuff is required since pigmented finish coatings are usually used and consequently relatively little dye is required. Garment leathers, suedes and nubucks on the other hand must be fully penetrated with dyestuff in order that cut edges or buffed surfaces show the same colour. In these cases very high offers of dyestuffs are used which may be up to 20% of the leather weight. In general, dyestuff offers used on leather are very much greater than those used to achieve an equivalent shade on many textile substrates. This is often true even of surface dyed leathers. The majority of leather dyes are anionic, of the acid and direct types. Fixation of these conventional leather dyes is favoured under acid conditions due to protonation of amino groups in the collagen matrix. The process of fixation is reversible and raising the pH of the leather causes stripping of the dyestuff. The dyeing mechanism involves salt linkages, hydrogen bonds, Van der Waal's bonds and other electrostatic attractions which are weak and easy to break. The weakness of these electrostatic attractions and the reversibility of the dyeing mechanism coupled with the very high dye offers used means that dyed leathers generally have very poor colour fastness properties, particularly when compared to some man-made fibres.

With leathers dyed to deep shades using high dye offers it is customary to use a cationic fixative as an after treatment to the dyeing process. These cationic fixatives form an insoluble complex with the anionic dyestuff in the leather structure which prevents dissolution of loose dyestuff. Use of these fixatives can, thus, significantly reduce dye migration as observed in static fastness tests such as IUF426 (Colour Fastness of Leather

WO 00/77292

PCT/GB00/02340

- to Perspiration) and IUF421 (Colour Fastness of Leather to Water). However, although these complexes have low aqueous solubility they are not chemically bound to the leather substrate and are frequently easily removed by rubbing, such as might occur during wear, resulting in transfer of colour to adjacent items of clothing, or during domestic
- 5 laundering processes. The complexes formed between the anionic dyestuffs and the cationic fixatives are also easily removed with organic solvents thus reducing the dry cleanability of the leather. Poor colour fastness of leather is a major quality issue for the leather industry being one of the most common sources of customer complaint.
- 10 One method which has been used to effect improvements in colour fastness of dyed leathers is through the use of reactive dyestuffs. These dyestuffs are essentially similar to conventional leather dyestuffs, being anionic, however, the one important difference is that they contain one or more groupings, integral with the dye molecule, which are capable of forming covalent bonds between the dye and the substrate. Use of these
- 15 materials has shown potential for producing dyed leathers with very high performance levels in terms of colour fastness. However, certain disadvantages are associated with the use of these dyes. Leather has a limited number of groups available in the collagen matrix with which the reactive dye can react. This means that it is generally only possible to achieve pale to medium depths of shade by means of covalent fixation and for deeper
- 20 shades it is necessary to revert to an anionic type acid fixation, which in general reduces the fastness properties.

- During the reactive dyeing process, as well as the reaction with the substrate, a competing reaction also occurs with the solvent, in this case water. This means that
- 25 some of the dyestuff is lost during the process, due to hydrolysis of the reactive groups, and is washed out into the effluent. As well as the obvious economic implications of losing part of the dye there are also serious environmental implications associated with this class of dye due to the hydrolysed dye polluting the effluent. This hydrolysed dyestuff has some affinity for leather, due to the cationic nature of the leather substrate,
- 30 which makes washing off extremely difficult. If this washing off process is not carried out effectively and some hydrolysed dye is allowed to remain in the leather, then this can give rise to poor wet fastness and the benefit of the covalently bonded dye is lost. These

WO 00/77292

PCT/GB00/02340

limitations have meant that reactive dyes have not found widespread usage within the leather industry.

Due to the low number of amine groups in the leather, only a limited amount of reactive dye can be covalently fixed. This means that reactive dyes cannot be used effectively for deep shades, e.g. black. The high level of customer complaints arising as a result of poor colour fastness of dyed leathers means there is a need for viable commercial processes capable of significantly improving fastness properties, particularly of fully dyed leathers of deep shades.

10

This invention is based on the finding that improved colour fastness, particularly for deep shades, can be achieved by treating leather with an aminosilane or aminosiloxane before dyeing .

15 Accordingly, in its broadest aspect the present invention provides a process for dyeing leather which comprises impregnating the leather with an aminosilane or aminosiloxane thereby providing additional dye sites in the collagen matrix for the dyestuff.

The aminosilane or aminosiloxane is typically applied to the leather as a pretreatment before dyeing, for example by drumming in an aqueous bath. After applying the aminosilane or aminosiloxane, the leather is preferably treated to extend the chain length of the impregnant, so as to enhance the immobilisation of the impregnant in the collagen matrix.

25 Typically the nature of aminosilanes is such that self-polymerisation to an aminosiloxane occurs in aqueous conditions, e.g. at pH above 7. Self-polymerisation may be initiated *in situ* after impregnation, as a pH adjustment step, or an oligomeric self-polymerised aminosiloxane may be used as the impregnant. Alternatively, or in addition, the leather may be heated, for example, during a drying step, to polymerise the aminosilane or
30 aminosiloxane. Increase of chain length may also be achieved by use of a cross-linking agent.

WO 00/77292

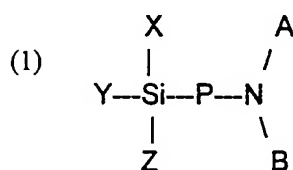
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- Aminosilanes and aminosiloxanes are available commercially as amino- or alkylamino-functionalised silanes or siloxanes (or silicones), so-called amino-oils. Typically an amino-oil has an amine number of at least 0.15, for example 0.15 to 3 or above. Suitable amino-siloxane oils include Wacker WR1600 (amine number 0.6) and Wacker L650 (amine number 3.0) and suitable amino-silanes include Wacker G91 and G95. The higher the amine number, the greater the number of additional dye sites that are provided. Suitable aminosilanes or aminosiloxanes include 3-(2-aminoethyl(amino)propyl trimethoxysilane and its self-condensation products.

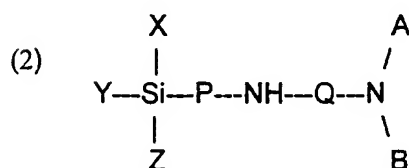
- 10 Compounds for use as the amino-functionalised silane or siloxane include those with any primary or secondary pendant amino group which will give a reaction with the reactive dye.

For example, compounds of formulae (1), (2) and (3) below may be used:

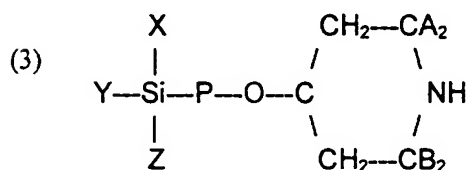
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(and analogs thereof containing more than one amino or substituted amino group)

- 35 in which X,Y,Z are each independently a C1-12 (especially C1-4) alkyl or alkoxy group, provided that at least one, and preferably at least two of X,Y,Z is alkoxy; A,B are each independently hydrogen or a C1-4 alkoxy group; and

WO 00/77292

PCT/GB00/02340

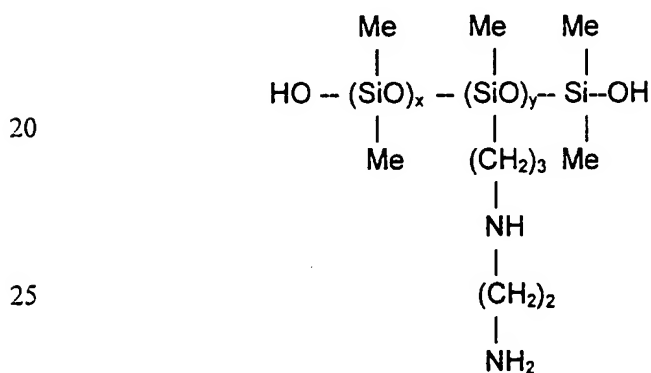
P, Q are each independently a C1-12 (typically C1-4) alkylene group.

Typically P and Q are ethylene or propylene linking groups. X, Y Z are suitably methyl, methoxy or ethoxy. A and B are preferably hydrogen, but may also be methyl, ethyl, propyl, etc.

In a useful class of commercially available compounds (for example from Wacker-Chemie) of formulae (1) and (2), P is propylene, Q is ethylene, A and B are hydrogen and X, Y, Z are trimethoxy or triethoxy, or X is methyl and Y, Z are dimethoxy or diethoxy. Suitable compounds are Wacker G91 and G95.

In compounds of formula (3), suitably A and B are dimethyl, and P is propylene. Compounds of this type are commercially available from Rhone Poulenc.

Suitable aminosiloxanes include compounds of structure:



Compounds of this type are commercially available, such as Wacker WR1600.

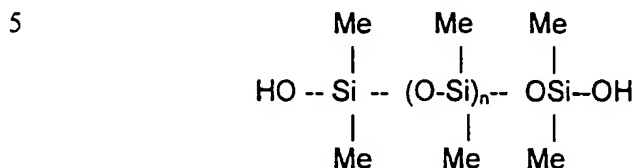
Typically x and y have values from 1 to 30 in commercially available materials.

In general aminosilanes or aminosiloxanes are preferred which can form large molecules by self-polymerisation. When this does not tend to occur due to the nature of the silane or siloxane, further crosslinking can be advantageous.

WO 00/77292

PCT/GB00/02340

Further increases in fastness may be effected by crosslinking with a second silicone such as an alpha-omega Si-OH functionalised polymer, typically a hydroxy-terminated silicone oil. For example hydroxy terminated silicones that may be used for crosslinking include silicone oils of structure:



such as Wacker X-PDM and X-601.

Alternatively the use of non-reactive hydrophobing agents, such as methyl hydrogen siloxanes, after impregnation with the aminosilane or aminosiloxane can also increase fastness. As hydrophobing agent, there can be used a methyl hydrogen siloxane, such as Wacker E10 and WS60E. Alternatives include water-based formulations based on silicones with functional groups that react with leather, for example carboxyl-silicones (available from BASF under the trade name Densodrin), mercapto-silicones and epoxy-silicones.

The aminosilane or aminosiloxane is held in the collagen matrix due to a variety of non-covalent bonding e.g. hydrogen bonding, Van der Waals' forces, ionic interactions (pH dependent) and other electrostatic interactions; the second silane or siloxane does not bond the aminosilane or aminosiloxane to collagen.

The dyestuff is typically a reactive dye which binds to the amino groups in the collagen and on the impregnant. Suitable reactive dyestuffs include those already in use in leather dyeing, such as acid dyes, mono- and dichlorotriazene dyes, vinylsulphone dyes and any conventional reactive dye that reacts with amines, e.g. CI-Reactive Black 5, CI-Reactive Black 8, CI-Reactive Blue 19, CI-Reactive Red 195, CI-Reactive Yellow 145.

After the aminosilane/siloxane treatments, the dyeing operation of this invention is based on conventional processing. Suitably the aminosilane or aminosiloxane is added as an oil

WO 00/77292

PCT/GB00/02340

or emulsion to a water bath, and the leather (optionally pre-neutralised and/or re-tanned) is added and drummed to achieve adequate penetration. If desired a pH adjustment may be made to initiate self-polymerisation. Alternatively or additionally, a second silane or siloxane is added for crosslinking or hydrophobing. The leather may then be drained and optionally washed and dried. The drying may be carried out at a temperature at which self-polymerisation is initiated or completed. Then the impregnated leather is returned to the bath, the reactive dyestuff is added and similarly drummed to fix the dyestuff onto the leather and the impregnant.

- 10 Once the leather has been treated with the aminosilane or aminosiloxane (with or without the second silane or siloxane), an increased amount of reactive dye is taken up by the leather (in comparison with non-treated leather) - for this no acidification is required. Thus not only is the fastness of the dyed leather improved, but the dyeing process is also assisted i.e. the treatment of leather with aminosilanes or aminosiloxanes is not an after-treatment to fix the dye, but a pre-treatment which significantly changes the dyeing property of the leather. Also the increased take up of dye from the bath results in a cleaner effluent, which is of significance for environmental issues.

20 In this dyeing process, the concentration of aminosilane or aminosiloxane added may be changed to suit the required colour strength. Also the concentration of the second silane or siloxane may be varied to affect the extent of cross-linking or polymerisation when using a reactive silicone such as a hydroxy functionalised silicone, or to affect the hydrophobic character in the case of a methyl hydroxy siloxane.

- 25 The processing pH may be adjusted to suit the type of reactive dye used. Also, the pH plays an important role in the extent of penetration of the aminosilane or aminosiloxane. At higher pH's (e.g. above 7) self polymerisation of the aminosilane or aminosiloxane may occur and the rate and extent of penetration of the resultant polyaminosiloxane is reduced. At lower pH's, e.g. around pH4, the amino groups become almost completely ionised and are held on to the leather surface via ionic interactions with the carboxyl groups in the collagen i.e. penetration is hindered due to ionic interactions. This can be used to preferentially maintain a higher amine concentration in the upper layer of the

WO 00/77292

PCT/GB00/02340

leather cross section, thus enabling higher fixation of the reactive dye in the surface layer of the leather.

The invention is illustrated by the following Examples.

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Example 1

(In the Examples all weights are expressed as a percentage of the weight of the leather to be dyed)

10

10% by wt. of 3-(2-aminoethyl(amino)propyl trimethoxysilane (Wacker G91) is added to 200% by wt. water. The solution is then added to neutralised leather and drummed in a dyeing vessel at 20 rpm, 55°C for 1 hour. The pH is adjusted to 8.5 with sodium bicarbonate and drummed for a further 60 minutes. The float is drained, the leather

15 washed once with 100% by wt. water (55°C, 20 rpm, 5 minutes) and then drained.

5% by wt. of a methyl hydrogen siloxane (Wacker WS60E) is added to 100% by wt. water. This is then added to the leather and drummed for 30 minutes. The float is drained and the leather may then be dried to facilitate cross-linking.

20

The leather is then dyed with 12% by wt. Reactive Black 5 for 2 hours at 55°C at 20 rpm. The float, which is practically devoid of dyestuff (over 98% dye uptake) is then drained and washed twice with 200% by wt. water.

25 The wash fastness, perspiration fastness and crock fastness were measured on the grey scale for the staining of adjacent fabric (cotton). Results are expressed in Grey Scale Units as staining of an adjacent cotton fabric. Grade 5 = no staining, Grade 1 = very stained, i.e. the higher the number, the better the fastness. The results were "4-5" for wash fastness, "5" for perspiration and "2-3" for wet crock fastness.

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WO 00/77292

PCT/GB00/02340

A control dyeing without the aminosilane and the siloxane gave similar fastness results, but the depth of shade (i.e. amount of dye in the substrate) was significantly lower and of little commercial value for unfinished leather.

5 **Example 2**

The procedures of Example 1 were repeated using different reactive dyes: CI – Reactive Black 5, CI – Reactive Black 8, CI – Reactive Blue 19, CI – Reactive Red 195 and CI – Reactive Yellow 145. In each case much improved dye uptake and colour fastness were
10 observed relative to the control.

Example 3

Example 1 was repeated by replacing 3-(2-aminoethyl(amino)propyltrimethoxysilane
15 with a prepolymerised aminosiloxane (Wacker L-650 - a dimethyl polysiloxane which contains aminoalkyl groups)

Examples 4 and 5

20 The procedures of Examples 1 and 3 respectively were repeated replacing the methylhydrogen siloxane with two different hydroxy-functionalised silicones (Wacker X-PDM and X-601).

WO 00/77292

PCT/GB00/02340

CLAIMS

1. A process for dyeing leather which comprises impregnating the leather with an aminosilane or aminosiloxane that provides additional dye sites in the collagen matrix for
5 the dyestuff.
2. A process according to claim 1 in which the aminosilane is 3-2-aminoethyl(amino)propyl trimethoxysilane, its siloxane product or a dimethyl polysiloxane with aminoethyl groups.
10
3. A process according to claim 1 or 2 in which the leather is treated to polymerise the aminosilane or aminosiloxane *in-situ*.
4. A process according to claim 3 in which the aminosilane or aminosiloxane is
15 induced to polymerise by a pH adjustment.
5. A process according to claim 3 or 4 in which the chain length of the aminosilane or aminosiloxane is increased by treatment with a cross-linking agent.
- 20 6. A process according to claim 5 in which the crosslinking agent is a hydroxy functionalised siloxane.
7. A process according to claim 1 or 2 in which the leather is also treated with a hydrophobing agent.
25
8. A process according to claim 7 in which the hydrophobing agent is a methyl hydrogen siloxane.
9. A process according to any of claims 1 to 8 in which the dyestuff is a reactive
30 dye.

WO 00/77292

PCT/GB00/02340

10. A process according to any one of claims 1 to 8 in which the dyestuff is an acid, direct, metal-complex, solubilised sulphur dye or mordant dye.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/02340

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D06P1/52 D06P3/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D06P C14C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BURKINSHAW S M ET AL: "CHITOSAN IN LEATHER PRODUCTION PART 3: BUILD-UP PROPERTIES OF CHITOSAN PRETREATED FULL-CHROME AND HEAVILY RETANNED LEATHER" JOURNAL OF THE SOCIETY OF LEATHER TECHNOLOGIES AND CHEMISTS, GB, NORTHAMPTON, vol. 76, 1992, pages 54-57, XP000490250 the whole document ---	1,10
A	US 3 832 203 A (SAUNDERS F ET AL) 27 August 1974 (1974-08-27) column 1, line 31 -column 2, line 36 example 1 ---	1,2,7
A	US 3 741 721 A (GAGLIARDI D) 26 June 1973 (1973-06-26) column 1, line 37 -column 11, line 45 --- -/--	1,10



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

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"&" document member of the same patent family

Date of the actual completion of the international search

6 October 2000

Date of mailing of the international search report

13/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

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Neugebauer, U

INTERNATIONAL SEARCH REPORT

Into International Application No
PCT/GB 00/02340

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 198241 Derwent Publications Ltd., London, GB; Class A87, AN 1982-87455E XP002149222 & SU 887 659 A (CONSUMER SERVICE EQ), 7 December 1981 (1981-12-07) abstract</p> <p>-----</p>	1,8-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

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SU 887659 A	07-12-1981	NONE	